



# Effects of ultrasound irradiation on the electrochemical treatment of wastes containing micelles

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## ABSTRACT

This work focuses on the effect of the irradiation of ultrasound during the electrolysis of wastes polluted with micelles. To do this, synthetic wastewater (emulating the ones produced in cosmetic industry) was formulated and it underwent several electrochemical and sono-electrochemical, at low and high frequencies, oxidation assays. Processes were monitored paying attention not only to the changes observed in the organic soluble intermediates and final products, but also to the size of the micelles. Results demonstrate that the presence of surfactant in wastes may interfere on the degradation of pollutants due to the formation of micelles. Nevertheless, 90% of mineralization was achieved by the coupled process of electrolysis and low frequency ultrasound. Furthermore, ultrasound irradiation can contribute to faster turbidity and foam depletion and to retard the formation of perchlorates. Regarding the micelles, it was found that application of ultrasound directly affects the changes on particles size during their destruction which, in turn, influences on the performance of the electrochemical process. A simple phenomenological model is proposed to explain the influence of this irradiation.

## 1. Introduction

Over the last decades, the electrolysis of wastewater has become a really interesting topic of study with hundreds of papers published and many reviews that summarize the state of the art in the technology [1–5]. From those works, it has been concluded that with the use of diamond coatings as anodes it is possible to improve the heterogeneous electrocatalytic process to treat very efficiently most of the pollutants that can be contained in wastewater. Mass transport has become the major handicap in the technology, in which promotion of mediated electrochemical oxidation processes and the improved mechanical design of electrochemical cells are the key paths to face this challenge. In particular, strategies based on the enlarging the electrocatalytic production of oxidants or activating them chemically, photo-chemically or sono-chemically are of interest according to the high number of paper published [6]. Thus, during the electrolytic treatment of wastes, it has been widely studied the electrochemical formation of oxidants such as hydrogen peroxide, ozone, peroxosulfates, peroxocarbonates, peroxophosphates and chlorine. Composition of the waste has a large influence on this production and operation conditions can help to modify it efficiently. Interactions of these oxidants among them in pure

electrochemical processes, and also with UV or US in combined treatments, lead to the formation of radicals such as the hydroxyl, sulfate, carbonate and chlorine. This cocktail of oxidants is responsible of the very strong oxidizing conditions produced in the bulk during the electrolysis, being its characterization one of the most interesting contributions to the catalytic understanding of the electrochemical treatments, because sometimes these interactions are synergistic and they contribute to improve the efficiency of the processes, while other they become antagonistic. Explanation is not always related to the nature of the pollutants to be degraded, but also to the composition of the waste and operation conditions applied which are the final responsible of the cocktail of oxidants formed. There are studies about this influence on soluble compounds but to the knowledge of the authors there are no studies focused on the treatment of more complex pollutant such as those present as micelles.

On the other hand, and coming back to additional ways of enhancing the performance of electrochemical processes, more recently, the application of concentration processes for pollutants solutions before the degradation is also becoming a very promising alternative [7–10], although this alternative is based on the minimization of the mass transfer problems that typically occurs in the electrochemical cell.

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Application of ultrasounds in combination with electrolysis has shown contradictory results, suggesting the very complex nature of the processes involved [11–16]. Synergetic effects are not observed in all works, and in some cases the application of US results in an antagonistic effect. At this point, it is important to highlight the difference between the application of low and high frequency ultrasounds [12,17–21]. Energy of the first type is not enough to promote the formation of oxidants by the rupture of molecules. Nevertheless, it promotes the so-called transient cavitation, in which the violent collapse of bubbles generates extreme conditions of temperature and pressure (hot-spot theory), where radicals such as hydroxyl ( $\cdot\text{OH}$ ), hydrogen ( $\cdot\text{H}$ ) and hydroperoxyl ( $\cdot\text{HO}_2$ ) can be produced. In addition to that, this effect improves the mixing conditions in the cell and, hence, it contributes to minimize the negative effect of mass transport control on the efficiency of the remediation process [12,21–23]. Opposite, energy of high-frequency ultrasound promotes the stable cavitation effect, in which bubbles collapses are less violent. Under those conditions, bubbles oscillate for longer times, which can improve the formation of radicals but does not improve physical effects [21,22,24]. However, when the formation of oxidants is huge (and combination of US and electrochemistry favor this formation), interactions between oxidants may contribute to deactivate them, making the process less efficient.

A very interesting topic of study in the use of electrolysis is the application of wastes which do not only contain soluble pollutants but also particulate pollutants. Presence of micelles in the waste is a case of very high interest, because several industrial wastewaters contain surfactants on their composition, which can interfere on the efficiency of the treatment. In addition, an important approach on remediation of soils is the soil-washing with surfactants, which simplifies the soil decontamination to a wastewater treatment problem [4]. In this context, the degradation of micelles during the treatment process is not well-studied, in particular paying attention to what happens with the size of the micelles and how this size affects to the efficiency of the treatment. Regarding electrochemical oxidation processes some previous works of our group have tried to shed light on the mechanisms [25–28], but there is a still a long way to have a clear model of the influence of ultrasound on the evolution of these species during the electrochemical degradation of wastes.

In order to go further in this topic, this work focuses on the degradation of a synthetic cosmetic waste, which contain not only soluble species but also micelles. In addition to discuss what happened during the electrolysis and sono-electrolysis with soluble organic and inorganic species, the work remarks the importance of the application of ultrasounds in the evolution of micelles and provides a simple mechanistic model to explain the differences between the application of low and high-frequently US. All this is studied in combination with the degradation of methyl-paraben, which is used not only as a model of hazardous pollutant (because of its well-known endocrine disruptor effects) but also as model of soluble aromatic pollutant. The electrolysis of this species in more simple wastes was evaluated in a previous work [29] and here we are going to expand conclusions to systems with a much more complex formulation.

## 2. Materials and methods

### 2.1. Chemicals and working solution

Synthetic wastewater (SW) containing high concentrations of organic matter was developed based on real effluents from cosmetic industries [30–33], in which methyl paraben is found. SW was prepared using a commercial micellar water solution (Agua Limpiadora Micelar, Delipius, Spain), in the concentration of  $5\text{ g L}^{-1}$ . To this solution,  $100\text{ mg L}^{-1}$  of methyl paraben and  $1\text{ g L}^{-1}$  of sodium dodecyl sulfate (SDS) were added, both from Sigma-Aldrich.

Characterization of the emulsion was based on COD measures (chemical oxygen demand), since the particulate matter would not be

**Table 1**

Amount of ions added to the working solution and initial ionic composition of the synthetic wastewater.

Ions	Concentration added ( $\text{mg L}^{-1}$ )	Total concentration in the SW ( $\text{mg L}^{-1}$ )
$\text{Cl}^-$	900	1000
$\text{SO}_4^{2-}$	160	430
$\text{PO}_4^{3-}$	13	40
$\text{Na}^+$	620	920
$\text{NH}_4^+$	26	28
$\text{Ca}^{+2}$	60	60
$\text{Mg}^{+2}$	20	40

accounted for TOC (total organic carbon) analysis (because all samples had to be filtered for carbon analysis). According to that, the micellar water (at the used concentration) represents a COD of  $510\text{ mgO}_2\text{ L}^{-1}$ , SDS represents about  $1350\text{ mgO}_2\text{ L}^{-1}$  and MeP contributes to about  $170\text{ mgO}_2\text{ L}^{-1}$ . At the end, SW prepared contains COD  $\sim 2000\text{ mgO}_2\text{ L}^{-1}$  and DOC  $\sim 400\text{ mgC L}^{-1}$ .

Besides the inorganic salts from the micellar water, additional salts were added to the emulsion, guaranteeing the presence of all ions that are common in cosmetic wastewater (Table 1) [30–33].  $\text{Na}_2\text{SO}_4$ , NaCl and  $\text{H}_2\text{SO}_4$  were purchased from Panreac,  $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$  from VWR Chemicals and  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$  from Sigma-Aldrich. Total concentration of each ion in the final synthetic wastewater is presented in Table 1 (a portion from the cosmetic micellar water and other added to the emulsion).

Chloroform (Sigma-Aldrich), sodium tetraborate decahydrate (VWR Chemicals) and methylene blue (Merck) were used for SDS determination. Acetonitrile, HPLC grade was obtained from VWR Chemicals. All solutions were prepared with high-purity water obtained from a Millipore Milli-Q system (resistivity  $> 18\text{ M cm}$  at  $25^\circ\text{C}$ ) and all reactants were used as received.

### 2.2. Experimental set-up

Experiments were carried out in a bench scale flow system described elsewhere [15]. A plate of boron doped diamond (BDD) and a plate of stainless steel were used as anode and cathode, respectively (both with surface area of  $75\text{ cm}^2$ ). A HQ-Power PS3010 power supply (0–30 V, 0–10 A) provided the applied current. A peristaltic pump (PERCOM-I, JP Selecta, Barcelona, Spain) was used to maintain the flow rate at  $7\text{ mL s}^{-1}$  and a thermostatic bath (Digitem 100, JP Selecta) to maintain 1 L of working solution at  $25^\circ\text{C}$  for 8 h of treatment. For the ultrasonic experiments an ultrasound probe was immersed in the glass tank directly acting in the wastewater. Tests were carried out at the acoustic frequencies of 20 kHz (UP200S, Hielscher Ultrasonics GmbH), 1 MHz and 10 MHz (EPOCH 650, Olympus), both equipment with nominal power of 200 W.

### 2.3. Analytical techniques

Methyl paraben was monitored by high performance liquid chromatography (Agilent Technologies 1260 chromatographer) with an Eclipse Plus C18 column ( $3.5\text{ }\mu\text{m}$   $4.6 \times 100\text{ mm}$ ), at  $25^\circ\text{C}$ , and UV detector set in 280 nm. Mobile phase was acetonitrile and water (60:40 v/v) with  $1\text{ mL min}^{-1}$  of flow rate. SDS was quantified according to the method described by Jurado et al. [34] using an Agilent Cary Series UV-vis spectrophotometer. Dissolved organic carbon (DOC) was determined in a Multi N/C 3100 Analytik Jena analyzer and turbidity was analyzed in a HI93703 microprocessor turbidimeter (HANNA Instruments). Inorganic anions ( $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ ) were measured by ion chromatography using a 930 Compact IC Flex (Metrohm). The samples for chromatography and carbon analysis (DOC) were previous filtered through a nylon

membrane (0.45  $\mu\text{m}$ ). Particle size was measured during the electrolysis of SW by laser diffraction analysis in a Mastersizer Hydro 2000SM (Malvern Panalytical).

#### 2.4. Electric energy per order

Energy consumption of the system was evaluated by electric energy per order according to Eq. 1 [35], where  $E_{\text{cell}}$  is the cell potential (V),  $t$  is time (h),  $V$  is the volume of treated solution (L) and  $C_0$  and  $C$  are the initial and final concentration of pollutant.

$$E_{\text{EO}} = \frac{E_{\text{cell}} \cdot t \cdot 1000}{V \cdot \log(C_0/C)} \quad (1)$$

### 3. Results and discussion

#### 3.1. Electrochemical treatment

A synthetic wastewater (SW) containing MeP and high concentration of micelles was developed and treated by electrochemical process. In order to observe the behavior of MeP under electrolytic process, the compound was firstly treated individually in sulfate and chloride media, which are the main anions present in the SW. Fig. 1 shows the removal of MeP in  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and SW, during electrolysis.

Methyl paraben is completely removed in all systems, however at different times: < 20 min, < 1 h and < 5 h in  $\text{Cl}^-$ , SW and  $\text{SO}_4^{2-}$ , respectively. These great differences are attributed to the main oxidant species generated in each medium. Faster removal in chloride medium is expected due to the chlorination of the organic molecule by active chlorine species, which are electrochemically generated ( $\text{Cl}_2$ ,  $\text{HClO}$  and  $\text{ClO}^-$ ) [1,36]. Hydroxyl radicals are also constantly formed in this medium, however they oxidize organic matter by slower mechanisms (H-abstraction and addition). Conversely, in sulfate medium, besides  $\cdot\text{OH}$  species, persulfate and sulfate radical anions ( $\text{SO}_4^{\cdot-}$ ) are also produced. These radicals are usually capable to oxidize several pollutants that are refractory towards  $\cdot\text{OH}$ , because they react predominantly by electron transfer. However, this mechanism is also slower than chlorination and, thus, slower MeP removal is observed [37,38].

Synthetic wastewater contains both  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  anions. Thus, all the previously mentioned oxidant species are expected to be formed. In fact, it is observed an intermediate behavior for MeP removal and the result is explained by the greater content of chloride than sulfate. Other authors also observed similar results using BDD anodes. Steter et al.

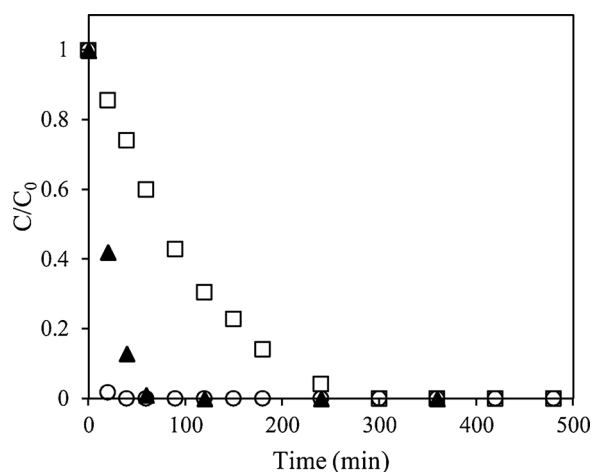


Fig. 1. Electrochemical removal of MeP (100  $\text{mg L}^{-1}$ ) in different media: (○) in 3.7  $\text{g L}^{-1}$  of NaCl, (□) in 3.0  $\text{g L}^{-1}$  of  $\text{Na}_2\text{SO}_4$  and (▲) in the synthetic wastewater.

Table 2

Removal of DOC by electrochemical process and its respective kinetic constants in all studied media.

	DOC removal (%)	$k_1$ ( $10^{-3} \text{ min}^{-1}$ )	$k_2$ ( $10^{-3} \text{ min}^{-1}$ )
$\text{Cl}^-$	100 (5 h)	3.9	13
$\text{SO}_4^{2-}$	100 (4 h)	7.4	15
SW	89 (8 h)	2.7	5.6

[39] compared sulfate and chloride anions as supporting electrolytes, individually and in combination, and found better mineralization results for the combined medium. Frontistis et al. [40] compared the removal of a pollutant in sulfate and in real wastewater, obtaining faster removal for the more complex matrix. They ascribed those results to the presence of other anions in the wastewater, which contribute to the formation of other oxidant species. Nevertheless, as it was described before, each specie acts through a different mechanism of oxidation, which favors the degradation of compounds of different nature. As a result of that, the oxidation of more organic species may occur, and the efficiency of the process increases.

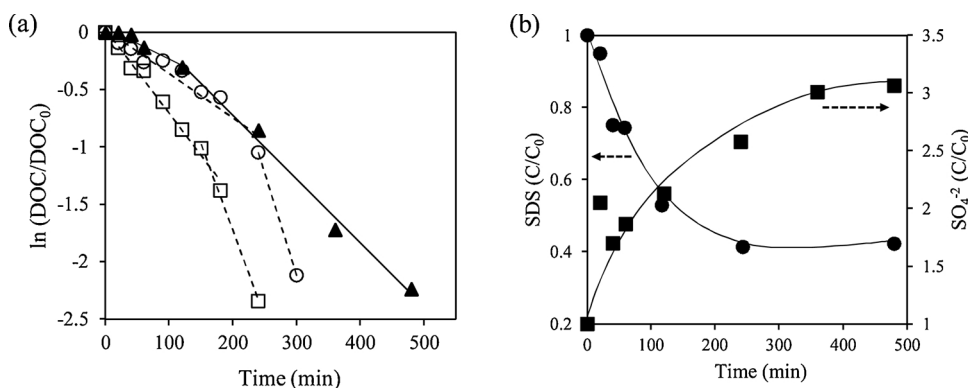
Although the removal of MeP was faster in chloride and SW media, the same is not observed for the total oxidation of organic matter. For the SW, 89% of DOC removal is achieved with 8 h of treatment, while for MeP in sulfate and chloride solutions 100% of DOC removal is achieved before 5 and 6 h, respectively. The complexity of the matrix decreases the kinetic of DOC removal and, thus, its mineralization efficiency (Table 2). Fig. 2a shows that mineralization, in all media, follows pseudo-first order kinetics with two distinctive regions, in which two kinetic constants can be determined:  $k_1$  and  $k_2$  for each regime, respectively (Table 2). The kinetic transitions observed are attributed to the nature of oxidants and intermediates generated in the medium, which results in different oxidation mechanisms during the process.

Regarding sulfate and chloride media, the difference on the mineralization efficiency is mostly due to the oxidation mechanism. As described before, MeP is rapidly converted to organochlorinated compounds under the presence of  $\text{HClO}/\text{ClO}^-$ . Those intermediates are very stable and more hardly degradable than in the case of sulfate medium, thus lower kinetic rate of mineralization is obtained. Although MeP oxidation in sulfate is slower, the mechanism of degradation consists in the rupture of carbon bonds, which facilitates further mineralization. On the other hand, a more complex kinetic is expected for SW degradation, due to the very high initial DOC and that organic matter is majorly found in the form of micelles. This means that part of the organic content is inside the particles, thus, not accessible to be immediately oxidized. Micelles need to be firstly attacked in order to continuously form smaller particles until their further rupture. At this point, the inner compounds are released to the bulk and can be consumed by the oxidant species.

It is important to note that the kinetic change on the SW oxidation curve, is not only explained by the intermediates formation. As the degradation of SDS proceeds, sulfate concentration increases with time, as showed in Fig. 2b. Previous works showed that the electrolysis of SDS promotes the releasing of sulfate anions, which can be oxidized to persulfate and improve the removal of organic compounds [41]. In fact, the kinetic transition occurs after 120 min of reaction, in which approximately 50% of SDS was consumed. Hence, the ratio  $[\text{SDS}]/[\text{SO}_4^{2-}]$  is significantly changed with regard to the initial ratio, and the oxidation kinetic of DOC is modified.

#### 3.2. Effect of ultrasound on electrolysis

As an attempt to improve the efficiency of the process, sonochemistry (SCh) and electrochemistry (ECh) technologies were coupled. Previous studies in our laboratory [42] evaluated the effect of ultrasound irradiation (US) to the oxidation of MeP in sulfate medium,



**Fig. 2.** a) Kinetics of electrochemical removal of DOC in different media: (○) MeP ( $100 \text{ mg L}^{-1}$ ) in  $3.7 \text{ g L}^{-1}$  of NaCl, (□) MeP in  $3.0 \text{ g L}^{-1}$  of  $\text{Na}_2\text{SO}_4$  and (▲) the synthetic wastewater. b) (●) removal of SDS in SW and (■) concentration of sulfate anions in SW during the electrolysis with  $30 \text{ mA cm}^{-2}$ .

**Table 3**

Kinetic constants of DOC removal of MeP ( $100 \text{ mg dm}^{-3}$ ) in sulfate medium ( $3.0 \text{ mg dm}^{-3}$ ) for electrochemical process with  $30 \text{ mA cm}^{-2}$  (E30) and the coupled processes with ultrasound at 20 kHz and 75% of power (L75), 1 MHz (H1) and 10 MHz (H10).

		E30	L75	H1	H10
$\text{SO}_4^{2-}$	$k_1 (10^{-3} \text{ min}^{-1})$	7.4	10	7.2	8.3
	$k_2 (10^{-3} \text{ min}^{-1})$	15	24	16	25

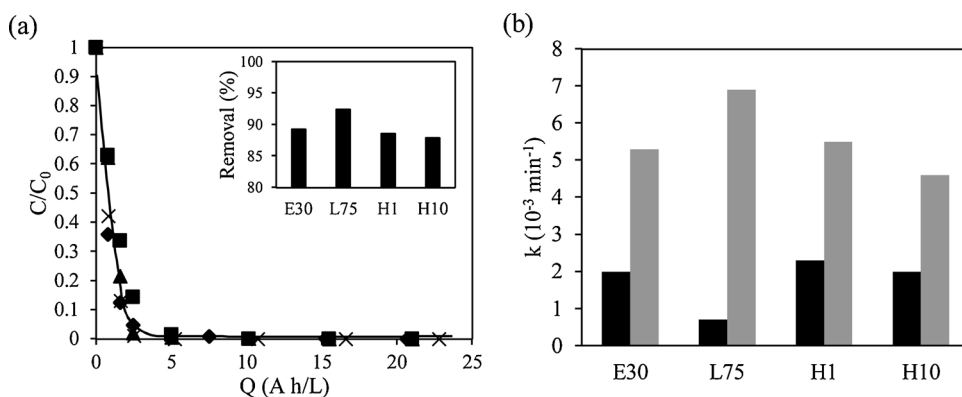
showing that the mineralization is favored by the coupled process (SECh process). The kinetic for dissolved organic carbon removal fitted a *pseudo*-first order with two regions, in which  $k_1$  and  $k_2$  are presented in Table 3. Under the condition L75, it was observed an improvement of 35% and 60% for  $k_1$  and  $k_2$ , respectively, and also, the complete mineralization was attained in 3 h compared to 4 h for electrochemical process. In addition to those results, it can be considered that SW is a much more complex matrix, in which ultrasound could present different effects. For instance, earlier researchers stated that the presence of surfactant can enhance the cavitation phenomenon by reducing the surface tension [17,22], which may improve the formation of radicals and, thus, the removal of pollutants.

According to that, ultrasound frequencies of 20 kHz, 1 MHz and 10 MHz were directly irradiated into the synthetic wastewater during electrolysis with  $30 \text{ mA cm}^{-2}$ . Fig. 3a shows MeP oxidation and the total removal of DOC (inset) after the applied processes. The abatement of MeP is not affected by the presence of ultrasound and complete removal is achieved by the time of 1 h ( $Q = 2.5 \text{ A h L}^{-1}$ ) under all studied conditions. However, previous studies found that single sonochemical process was capable to remove, approximately, 30% of MeP, when low frequency ultrasound was used [42]. In SW, none of the frequencies applied were efficient to oxidize methyl paraben without the combination to electrolysis (not shown), which is possibly a consequence of the higher complexity of the medium. Inset of Fig. 3a shows the

elimination of DOC after 8 h of treatment and the respective kinetic constants are presented on Fig. 3b. Similar behavior was observed for the kinetic of DOC abatement in the presence and absence of US, in which  $k_2$  is much higher than  $k_1$ . Low frequency enhanced the removal in the second kinetic region, however,  $k_1$  was smaller than in ECh process and the total removal was not favored. Although the attained DOC removals are very similar and not much should be stated, the observed tendency is consistent with the results obtained in previous work for the degradation of MeP in sulfate medium:  $\text{L75} > \text{H1} > \text{H10}$  [42]. This could indicate that ultrasound does may improve electrochemical removal of organic matter. However, the applied conditions might not be ideal.

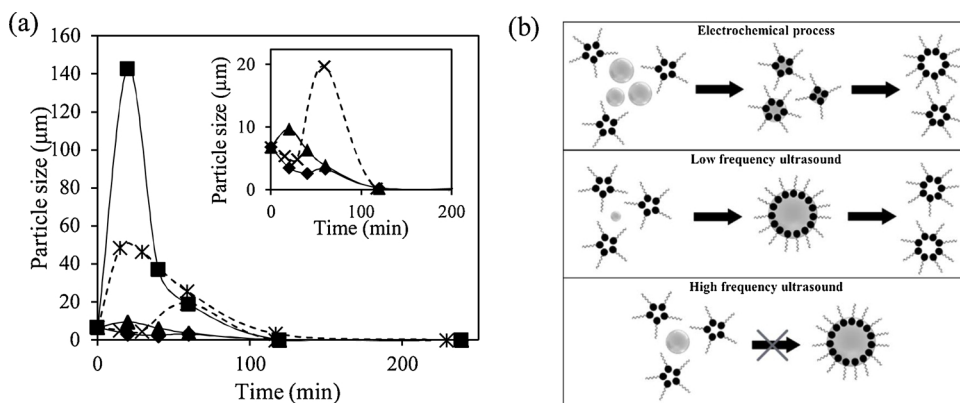
At this point, in order to better understand the effects of ultrasound in this system, it is important to verify the behavior of micelles in the emulsion. For that, particle size was monitored during the electrolysis with and without US irradiation (Fig. 4a). It was expected that, as the degradation proceeds, micelles would be attacked, promoting a decrease on their size until the rupture, as it was found by Santos, et al. [26]. However, it is observed, for all conditions, an increase on the size of the micelles before their decrease. It was recently reported that micelle size evolution is an interfacial phenomenon strongly dependent on the solution agitation, due to the formation of air/water interfaces [43]. Under the applied conditions, electrolysis generates high concentration of gases (oxygen and chlorine), resulting in a huge amount of bubbles and great stirring of the emulsion. This effect is responsible for the increasing on particle size as proposed on Fig. 4b. Surfactant molecules will form micelles, which in the presence of gas bubbles will incorporate these, initiating the growth process; surfactant molecules adsorb to the air/water interfaces may produce bigger micelles by coalescence. Moreover, when current density is doubled (to  $60 \text{ mA cm}^{-2}$ ) for ECh process, particles size increase 2.5 times and the time in which the phenomenon occurs is 3 times shortened, which is explained by the even more intense generation of gases in the medium.

A recent study showed that ultrasound can accelerate micelle growth by an order of magnitude with respect to agitation by vortex



**Fig. 3.** a) Removal of MeP ( $100 \text{ mg L}^{-1}$ ) in synthetic wastewater and by (×) ECh ( $30 \text{ mA cm}^{-2}$ ) and SECh processes (■) 20 kHz, 75% power (L75), (▲) 1 MHz (H1) and (◆) 10 MHz (H10). Inset: Removal of DOC after 8 h of ECh and SECh treatments. b) kinetic constants, (black)  $k_1$  and (gray)  $k_2$ , for DOC removal.





**Fig. 4.** a) Determination of micelles size during the oxidation of the synthetic wastewater. Electrochemical process with (X) 30 mA cm<sup>-2</sup> and (\*) 60 mA cm<sup>-2</sup>, and SECh processes: (■) 20 kHz, (▲) 1 MHz and (◆) 10 MHz, with 30 mA cm<sup>-2</sup>. Inset: Zoom of the curves E30, H1 and H10; b) scheme of the proposed effect of air bubbles on the micelles without any cavitation effect, under transient cavitation and under stable cavitation based on Scheme 1 from Lokupitiya, et al. [44].

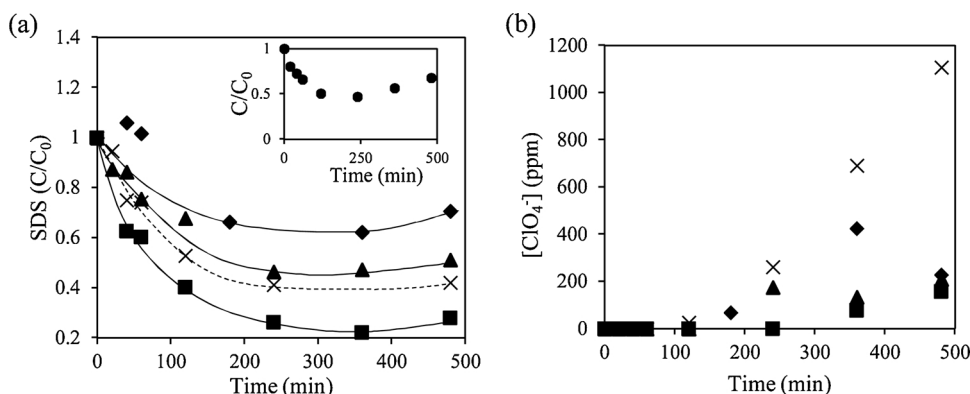
[44]. Cavitation effect enhance the production of bubbles, which increases the interfaces air/water. In addition, US acts on electro-generated gas bubbles, promoting their faster rupture, which contributes to micelles evolution (Fig. 4b). The growth of cavitation bubbles promotes the fast adsorption of micelles on the interface; the further collapse will lead to a reorganization of the surfactants and the inner content of micelles (hydrophobic compounds), in which higher particles may be formed. In fact, it is possible to see that under the presence of 20 kHz ultrasound (L75), particle size increased more than 7 times with relation to E30, and the time of maximum size decreased by half. According to this, it is possible to explain the kinetic of DOC removal observed on Fig. 3b for L75. Due to the large micelle size, it is more difficult to break these particles and release organic compounds into the bulk for oxidation, thus, the initial kinetic rate ( $k_1$ ) is the lowest. However, after 120 min of treatment, no more particles are detected, which means that all compounds are dissolved in the solution and can be oxidized. At this point,  $k_2$  increases for all conditions, being the effect more remarkable for L75, that is almost 10 times greater than  $k_1$  and is 30% higher than E30  $k_2$ .

Low frequency ultrasound promotes an effect known as transient cavitation, in which generated bubbles are unstable and their collapse is very rapid and violent. As a result, great amount of energy is released, producing extreme conditions in which  $\cdot\text{OH}$  radicals and  $\text{H}_2\text{O}_2$  can be formed by water sonolysis (Eqs. 2 and 3). In addition to those, species such as  $\text{Cl}^\cdot$  and  $\text{SO}_4^{\cdot-}$  can also be produced from chlorine and persulfate anions (Eqs. 4 and 5), contributing to the oxidation of organic compounds [22,45,46]. At high concentration of micelles, the produced bubbles are surrounded by particles; at the point of their collapse the energy released contributes to the reorganization of micelles, inhibiting the sonochemical effect of production of radicals. After the removal of particles, at 120 min, kinetic constant of DOC removal on L75 increases due to the cavitation contribution to the oxidation.



On the other hand, inset of Fig. 4a shows that the micelles growth happens in a smaller scale when 1 and 10 MHz are applied. High frequency ultrasound promotes a stable cavitation, in which bubbles oscillation is slow, resulting in a higher lifetime and a non-violent collapse [21,22]. This may be the explanation for the smaller size of micelles observed for H1 and H10 tests. Under those conditions, it seems that US acts on the electrogeneration of gas bubbles, promoting their oscillation for a longer period and inhibiting the evolution of micelles size (Fig. 4b). This effect is still unclear and more studies should be carried out in order to elucidate its mechanism. Anyhow, those results are also in agreement with the kinetic constants presented in Fig. 3b, in which the difference between E30 and high frequency experiments (H1 and H10) is not remarkable. Even after the removal of particles, the stable cavitation phenomenon does not favor the formation of radicals, and no improvement is achieved on oxidation. Nevertheless, considering that 1 MHz is the boundary between low and high frequency ultrasound, both cavitation effects will take place at certain levels, hence, a small increase on particle size is observed at the first 10 min of degradation. This is in agreement with the previous findings [42], in which the synergistic effect of coupling US and ECh process followed the order: L75 > H1 > H10.

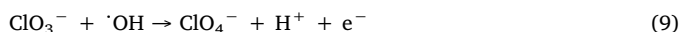
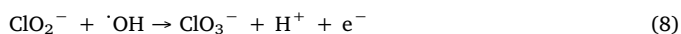
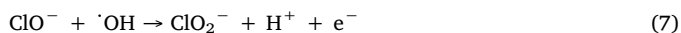
Fig. 5a shows the degradation of SDS by ECh and SECh process. As already mentioned, SDS molecules are majorly found in the form of micelles. The presence of oxidants, will promote the degradation of SDS without breaking the particles, in a first moment. This is consistent with the first hours of treatment, in which SDS concentration decreases. However, it is observed a point in which the concentration of SDS slightly increase, approximately about 5 h of treatment. In order to confirm this behavior, an electrochemical test was carried out at 60 mA



**Fig. 5.** a) Removal of SDS (1 g L<sup>-1</sup>) and b) formation of perchlorate by (X) ECh (30 mA cm<sup>-2</sup>) and SECh processes (■) 20 kHz, 75% power, (▲) 1 MHz and (◆) 10 MHz. Inset: Electrochemical removal of SDS using 60 mA cm<sup>-2</sup>.

$\text{cm}^{-2}$  (inset), where the effect can be clearly seen. These results suggest that SDS concentration decreases, in a first moment, not only by its degradation, but also by a physical process. It was possible to observe the formation of foam during the oxidation processes which means that SDS is being removed from the emulsion. As the degradation proceeds, micelles are removed and the concentration of SDS decreases in solution; this promotes the dissolution of foam and the migration of SDS back to solution, rising its concentration. Regarding US effect, as expected, L75 showed better results on SDS oxidation and removal of foam. In fact, this was the only condition in which none foam was observed at the end of the treatment, as will be further discussed.

On Fig. 5b is presented the production of perchlorate anions in each system. As it is well known, the formation of  $\text{ClO}_4^-$  is a consequence of the use of diamond anodes in chloride medium (Eqs. 6–9). The application of US delayed its formation in more than 1 h for the condition L75 and the final concentration is 7 times lower than for electrochemical process. This is an important result considering that perchlorate is very harmful to human health and ecosystems [1,47].



For processes with first-order rate constants, it is possible to determine the necessary energy to degrade the contaminant by one order of magnitude, according to Eq. 1. Table 4 compares the electric energy per order of organic matter removal for the electrochemical process individually and coupled to ultrasound. At this point it is clear that, due to the high content of micelles on the SW emulsion, its treatment consists on several effects, such as effective stirring, production and dissolution of foam, reorganization of micelles, varying its size, rupture of micelles, elimination of particles and oxidation of organic compounds. Considering this, energy consumption is even more interesting, because involves the necessary energy for both physical and chemical processes. At low frequency (L75), less energy was required to achieve complete mineralization, which means that the oxidation process is more efficient. As discussed before, this is mainly due to the higher generation of oxidants under the presence of transient cavitation.

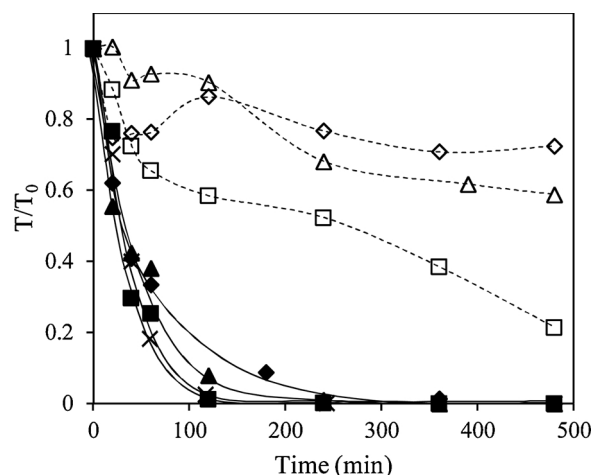
As mentioned at the beginning, the developed SW is a white silky emulsion, allowing the study of micelles behavior under electrochemical treatment and irradiation of ultrasound. Hence, it is also important to consider the physical aspect of the treated wastewater. SDS promotes the aggregation of particles and, as a consequence, the initial turbidity of SW was very high ( $\sim 500$  FTU).

Fig. 6 shows the depletion of turbidity during the treatments. It can be seen that irradiation of ultrasound directly affects the physical aspect of the wastewater; the lower the frequency, the faster is the decrease on the turbidity. This results are better seen on the experiments without current application. As discussed before, violent cavitation is resulted from the application of high intensity acoustic field (low frequency), and, under this condition, the bubbles can act as mechanical forces, which can induce the aggregation or disaggregation of particles [48].

**Table 4**

Energy consumption per order of DOC removal for electrochemical process with  $30 \text{ mA cm}^{-2}$  (E30) and the coupled processes with ultrasound at 20 kHz (L75), 1 MHz (H1) and 10 MHz (H10).

Experiment	$E_{\text{EO}}$ (kWh/m <sup>3</sup> /order)
E30	63
L75	51
H1	64
H10	66



**Fig. 6.** Removal of turbidity by (x) ECh ( $30 \text{ mA cm}^{-2}$ ), (empty symbols) SCh and (full symbols) SECh processes. (■) 20 kHz, 75% power, (▲) 1 MHz and (◆) 10 MHz.

This last effect is related to the decrease of turbidity and might facilitate the degradation of organic matter, by increasing the surface area of the particles. As the acoustic intensity decreases, transient cavitation turns to stable cavitation and the collapse of the bubbles is less powerful. As a result, disaggregation of particles is not promoted and turbidity takes more time to be removed.

Another physical aspect of the solution that needs to be taken into account is the formation of foam in the glass tank, during the applied treatments for the SW, mentioned before. This was an expected outcome, considering the high concentration of SDS under the circulation of solution and the electro evolution of gases. The dissolution of this foam was observed and after the 8 h, its remaining quantity in the reservoir was different for each treatment. It was not possible to measure the reminiscent amount of foam, however, some important aspects were noted: in SCh processes, a clear final solution was obtained after using 20 kHz, while for the other frequencies the final samples were still white turbid; for ECh and SECh processes, the final solutions were clear, however only with 20 kHz there was no foam at the end of the experiment. These observations reinforce that low frequency ultrasound was the better choice to combine with electrolysis for the studied system. At this point, it is possible to state that although ultrasound did not promote a huge improvement in the chemical oxidation of the wastewater, it does improve the physical aspect of it, which is also important to consider for the disposable of effluents.

#### 4. Conclusions

From this work, the following conclusions can be drawn:

- Electrochemical process with diamond electrodes is efficient for the treatment of cosmetic industry wastewater, attaining almost 90% of mineralization in 8 h.
- The presence of surfactants in the wastewater interferes on the degradation of pollutants. High concentrations of micelles may make more complex the oxidation of hydrophobic organic compounds, since they are only released to the aqueous phase after the micelles rupture.
- Ultrasound did not improve electrochemical oxidation. In a complex wastewater, ultrasound energy will firstly promote physical processes, such as particle size growth and depletion of turbidity and foam, before it contributes to chemical effects (activation of oxidants).
- Under great content of micelles, high evolution of bubbles may promote the coalescence of micelles. Cavitation of low-frequency

ultrasound helps to rearrange micelles into larger particles, which interferes on their stability and may facilitate the degradation.

Besides the work showed important results regarding the effect of surfactant in wastewater and the behavior of micelles under electrochemical and sonochemical treatments, there is still room for this topic. Some additional research with hydrophobic pollutants needs to be explored, in order to better understand the possible interfering effects of surfactants and micelles on wastewater.

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